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Review of the article "On the Equilibrium of Heterogeneous Substances", which was published in "Transactions of the Connecticut Academy of Arts and Sciences", vol. 3 (1874-78), pp. 108-248 and 343-524.

1877 gründete Leo Koenigsberger gemeinsam mit Gustav Zeuner die Zeitschrift *Repertorium der literarischen Arbeiten aus dem Gebiete der reinen und angewandten Mathematik*, die Mathematikern die Möglichkeit bot, ihre neuen Publikationen in Eigenreferaten vorzustellen.

Le Livre II est consacré aux applications analytiques du Calcul infinitésimal.

Le premier Chapitre traite du développement des fonctions en séries, et se termine par un complément aux éléments de la théorie des quantités complexes, où sont definies les fonctions exponentielles et circulaires de ces quantités.

Le Chapitre II a pour objet les applications analytiques de la différentiation: Détermination des vraies valeurs; maxima et minima; décomposition des fonctions rationnelles en fractions simples.

Le Chapitre III contient le développement et l'application des méthodes d'intégration indiquées dans le Livre Ier; l'étude des cas singuliers des intégrales définies; la différentiation et l'intégration sous le signe $\int$, avec l'emploi de ces opérations dans le calcul des intégrales définies spéciales; le changement de variables dans les intégrales multiples; les propriétés les plus simples des intégrales eulériennes, et la formule de Maclaurin pour le calcul approché des intégrales définies.

Les deux volumes suivants contiendront les quatre derniers Livres, qui traiteront successivement des applications de l'Analyse infinitésimale à la Géométrie, des équations différentielles ordinaires, des équations aux dérivées partielles, des fonctions d'une variable complexe, et des éléments de la théorie des fonctions elliptiques. Le tome II est sous presse.

Bordeaux. J. Hoüel.

J. Willard Gibbs: On the Equilibrium of Heterogeneous Substances. (Transactions of the Connecticut Academy of Arts and Sciences, vol. III. pp. 108—248 and 343—524. 1876—1878.)

It is an inference naturally suggested by the general increase of entropy which accompanies the changes occurring in any isolated material system that when the entropy of the system has reached a maximum, the system will be in a state of equilibrium. Although this principle has by no means escaped the attention of physicists, its importance does not appear to have been duly appreciated. Little has been done to develop the principle as a foundation for the general theory of thermodynamic equilibrium.

The principle may be formulated as follows, constituting a criterion of equilibrium:

I. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.*

The following form, which is easily shown to be equivalent to the preceding, is often more convenient in application:

II. *For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive.*

If we denote the energy and entropy of the system by ε and η respectively, the criterion of equilibrium may be expressed by either of the formulæ

(1) $$(\delta\eta)_\varepsilon \leqq 0,$$

(2) $$(\delta\varepsilon)_\eta \geqq 0.$$

Again, if we assume that the temperature of the system is uniform, and denote its absolute temperature by t, and set

(3) $$\psi = \varepsilon - t\eta,$$

the remaining conditions of equilibrium may be expressed by the formula

(4) $$(\delta\psi)_t \geqq 0,$$

the suffixed letter, as in the preceding cases, indicating that the quantity which it represents is constant. This condition, in connection with that of uniform temperature, may be shown to be equivalent to (1) or (2). The difference of the values of ψ for two different states of the system which have the same temperature represents the work which would be expended in bringing the system from one state to the other by a reversible process and without change of temperature.

If the system is incapable of thermal changes, like the systems considered in theoretical mechanics, we may regard the entropy as having the constant value zero. Conditions (2) and (4) may then by written

$$\delta\varepsilon \geqq 0, \qquad \delta\psi \geqq 0,$$

and are obviously identical in signification, since in this case $\psi = \varepsilon$.

Conditions (2) and (4), as criteria of equilibrium, may therefore both be regarded as extensions of the criterion employed in ordinary statics to the more general case of a thermodynamic sy-

stem. In fact, each of the quantities $-\varepsilon$ and $-\psi$ (relating to a system without sensible motion) may by regarded as a kind of force-function for the system, — the former as the force-function *for constant entropy* (i. e., when only such states of the system are considered as have the same entropy), and the latter as the force-function *for constant temperature* (i. e., when only such states of the system are considered as have the same uniform temperature).

In the deduction of the particular condition of equilibrium for any system, the general formula (4) has an evident advantage over (1) or (2) with respect to the brevity of the processes of reduction, since the limitation of constant temperature applies to every part of the system taken separately, and diminishes by one the number of independent variations in the state of these parts which we have to consider. Moreover, the transition from the systems considered in ordinary mechanics to thermodynamic systems is most naturally made by this formula, since it has always been customary to apply the principles of theoretical mechanics to real systems on the supposition (more or less distinctly conceived and expressed) that the temperature of the system remains constant, the mechanical properties of a thermodynamic system maintained at a constant temperature being such as might be imagined to belong to a purely mechanical system, and admitting of representation by a force-function, as follows directly from the fundamental laws of thermodynamics.

Notwithstanding these considerations, the author has preferred in general to use condition (2) as the criterion of equilibrium, believing that it would be useful to exhibit the conditions of equilibrium of thermodynamic systems in connection with those quantities which are most simple and most general in their definitions, and which appear most important in the general theory of such systems. The slightly different form in which the subject would develop itself, if condition (4) had been chosen as a point of departure instead of (2), is occasionally indicated.

Equilibrium of masses in contact. — The first problem to which the criterion is applied is the determination of the conditions of equilibrium for different masses in contact, when uninfluenced by gravity, electricity, distortion of the solid masses, or capillary tensions. The statement of the result is facilitated by the following definition.

If to any homogeneous mass in a state of hydrostatic stress

we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the *potential* for that substance in the mass considered.

In addition to equality of temperature and pressure in the masses in contact, it is necessary for equilibrium that the potential for every substance which is an independently variable component of any of the different masses shall have the same value in all of which it is such a component, so far as they are in contact with one another. But if a substance, without being an actual component of a certain mass in the given state of the system, is capable of being absorbed by it, it is sufficient if the value of the potential for that substance in that mass is not less than in any contiguous mass of which the substance is an actual component. We may regard these conditions as sufficient for equilibrium with respect to infinitesimal variations in the composition and thermodynamic state of the different masses in contact. There are certain other conditions which relate to the possible formation of masses entirely different in composition or state from any initially existing. These conditions are best regarded as determining the stability of the system, and will be mentioned under that head.

Anything which restricts the free movement of the component substances, or of the masses as such, may diminish the number of conditions which are necessary for equilibrium.

Equilibrium of osmotic forces. — If we suppose two fluid masses to be separated by a diaphragm which is permeable to some of the component substances and not to others, of the conditions of equilibrium which have just been mentioned, those will still subsist which relate to temperature and the potentials for the substances to which the diaphragm is permeable, but those relating to the potentials for the substances to which the diaphragm is impermeable will no longer be necessary. Whether the pressure must be the same in the two fluids will depend upon the rigidity of the diaphragm. Even when the diaphragm is permeable to all the components without restriction, equality of pressure in the two fluids is not always necessary for equilibrium.

Effect of gravity. — In a system subject to the action of gravity, the potential for each substance, instead of having a uniform value throughout the system, so far as the substance actually

occurs as an independently variable component, will decrease uniformly with increasing height, the difference of its values at different levels being equal to the difference of level multiplied by the force of gravity.

Fundamental equations. — Let ε, η, v, t and p denote respectively the energy, entropy, volume, (absolute) temperature, and pressure of a homogeneous mass, which may be either fluid or solid, provided that it is subject only to hydrostatic pressures, and let $m_1, m_2, \ldots m_n$ denote the quantities of its independently variable components, and $\mu_1, \mu_2, \ldots \mu_n$ the potentials for these components. It is easily shown that ε is a function of η, v, m_1, $m_2, \ldots m_n$, and that the complete value of $d\varepsilon$ is given by the equation.

$$(5) \qquad d\varepsilon = t d\eta - p dv + \mu_1 dm_1 + \mu_2 dm_2 \cdots + \mu_n dm_n.$$

Now if ε is known in terms of $\eta, v, m_1, \ldots m_n$, we can obtain by differentiation $t, p, \mu_1, \ldots \mu_n$ in terms of the same variables. This will make $n + 3$ independent known relations between the $2n + 5$ variables, $\varepsilon, \eta, v, m_1, m_2, \ldots m_n, t, p, \mu_1, \mu_2, \ldots \mu_n$. These are all that exist, for of these variables, $n + 2$ are evidently independent. Now upon these relations depend a very large class of the properties of the compound considered, — we may say in general, all its thermal, mechanical, and chemical properties, so far as *active tendencies* are concerned, in cases in which the form of the mass does not require consideration. A single equation from which all these relations may be deduced may be called a fundamental equation. An equation between $\varepsilon, \eta, v, m_1, m_2, \ldots m_n$ is a fundamental equation. But there are other equations which possess the same property.

If we suppose the quantity ψ to be determined for such a mass as we are considering by equation (3), we may obtain by differentiation and comparison with (5)

$$(6) \quad d\psi = -\eta dt - p dv + \mu_1 dm_1 + m_2 dm_2 + \cdots + \mu_n dm_n.$$

If, then, ψ is known as a function of $t, v, m_1, m_2, \ldots m_n$, we can find $\eta, p, \mu_1, \mu_2, \ldots \mu_n$ in terms of the same variables. If we then substitute for ψ in our original equation its value taken from equation (3) we shall have again $n + 3$ independent relations between the same $2n + 5$ variables as before.

Let

$$(7) \qquad \zeta = \varepsilon - t\eta + pv,$$

then, by (5),

$$(8)\qquad d\zeta = -\eta dt + vdp + \mu_1 dm_1 + \mu_2 dm_2 \cdots + \mu_n dm_n.$$

If, then, ζ is known as a function of t, p, m_1, $m_2 \ldots m_n$, wen can find η, v, μ_1, μ_2, $\ldots \mu_n$ in terms of the same variables. By eliminating ζ, we may obtain again $n+3$ independent relations between the same $2n+5$ variables as at first.*)

If we integrate (5), (6) and (8), supposing the quantity of the compound substance considered to vary from zero to any finite value, its nature and state remaining unchanged, we obtain.

$$(9)\qquad \varepsilon = t\eta - pv + \mu_1 m_1 + \mu_2 m_2 + \cdots + \mu_n m_n$$

$$(10)\qquad \psi = -pv + \mu_1 m_1 + \mu_2 m_2 + \cdots + \mu_n m_n,$$

$$(11)\qquad \zeta = \mu_1 m_1 + \mu_2 m_2 + \cdots + \mu_n m_n.$$

If we differentiate (9) in the most general manner, and compare the result with (5), we obtain

$$(12)\qquad -vdp + \eta dt + m_1 d\mu_1 + m_2 d\mu_2 + \cdots + m_n d\mu_n = 0,$$

or

$$(13)\qquad dp = \frac{\eta}{v} dt + \frac{m_1}{v} d\mu_1 + \frac{m_2}{v} d\mu_2 + \cdots + \frac{m_n}{v} d\mu_n = 0.$$

Hence, there is a relation between the $n+2$ quantities t, p, μ_1, μ_2, $\cdots \mu_n$, which, if known, will enable us to find in terms of these quantities all the ratios of the $n+2$ quantities η, v, m_1, m_2, $\cdots m_n$. With (9), this will make $n+3$ independent relations between the same $2n+5$ variables as at first.

Any equation, therefore, between the quantities

	ε,	η,	v,	m_1,	$m_2, \ldots m_n$,
or	ψ,	t,	v,	m_1,	$m_2, \ldots m_n$,
or	ζ,	t,	p,	m_1,	$m_2, \ldots m_n$,
or		t,	p,	μ_1,	$\mu_2, \ldots \mu_n$,

*) The properties of the quantities $-\psi$ and $-\zeta$ regarded as functions of the temperature and volume, and temperature and pressure, respectively, the composition of the body being regarded as invariable, have been discussed by M. Massieu in a memoir entitled "Sur les fonctions carractéristiques des divers fluids et sur la théorie des vapeurs" (*Mém. Savants Etrang.* t. xxii.) A brief sketche of his method in a form slightly different from that ultimately adopted is given in *Comptes Rendus* t. lxix, (1869) pp. 858 and 1057, and a report on his memoir by M. Bertrand in *Comptes Rendus*, t. lxxi, p. 257. M. Massieu appears to have been the first to solve the problem of representing all the properties of a body of invariable composition which are concerned in reversible processes by means of a single function.

is a fundamental equation, and any such is entirely equivalent to any other.

Coëxistent phases. — In considering the different homogeneous bodies which can be formed out of any set of component substances, it is convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its size or form. The word *phase* has been chosen for this purpose. Such bodies as differ in composition or state are called different phases of the matter considered, all bodies which differ only in size and form being regarded as different examples of the same phase. Phases which can exist together, the dividing surfaces being plain, in an equilibrium which does not depend upon passive resistances to change, are called *coëxistent*.

The number of independent variations of which a system of coëxistent phases is capable is $n + 2 - r$, where r denotes the number of phases, and n the number of independently variable components in the whole system. For the system of phases is completely specified by the temperature, the pressure, and the n potentials, and between these $n + 2$ quantities there are r independent relations (one for each phase), which characterize the system of phases.

When the number of phases exceeds the number of components by unity, the system is capable of a single variation of phase. The pressure and all the potentials may be regarded as functions of the temperature. The determination of these functions depends upon the elimination of the proper quantities from the fundamental equations in p, t, μ_1, μ_2, etc. for the several members of the system. But without a knowledge of these fundamental equations, the values of the differential co-efficients such as $\frac{dp}{dt}$ may be expressed in terms of the entropies and volumes of the different bodies and the quantities of their several components. For this end we have only to eliminate the differentials of the potentials from the different equations of the form (12) relating to the different bodies. In the simplest case, when there is but one component, we obtain the wellknown formula

$$\frac{dp}{dt} = \frac{\eta' - \eta''}{v' - v''} = \frac{Q}{t(v'' - v')},$$

in which v', v'', η', η'', denote the volumes and entropies of a given quantity of the substance in the two phases, and Q the heat which it absorbs in passing from one phase to the other.

It is easily shown that if the temperature of two coëxistent phases of two components is maintained constant, the pressure is in general a maximum or minimum when the composition of the phases is identical. In like manner, if the pressure of the phases is maintained constant, the temperature is in general a maximum or minimum when the composition of the phases is identical. The series of simultaneous values of t and p for which the composition of two coëxistent phases is identical separates those simultaneous values of t and p for which no coëxistent phases are possible from those for which there are two pairs of coëxistent phases.

If the temperature of three coëxistent phases of three components is maintained constant, the pressure is in general a maximum or minimum when the composition of one of the phases is such as can be produced by combining the other two. If the pressure is maintained constant, the temperature is in general a maximum or minimum when the same condition in regard to the composition of the phases is fulfilled.

Stability of fluids. — A criterion of the stability of a homogeneous fluid, or of a system of coëxistent fluid phases, is afforded by the expressirn

$$\varepsilon - t'\eta + p'v - \mu_1' m_1 - \mu_2' m_2 - \cdots - \mu_n' m_n \tag{14}$$

in which the values of the accented letters are to be determined by the phase or system of phases of which the stability is in question, and the values of the unaccented letters by any other phase of the same components, the possible formation of which is in question. We may call the former constants, and the latter variables. Now if the value of the expression, thus determined, is always positive for any possible values of the variables, the phase or system of phases will be stable with respect to the formation of any new phases of its components. But if the expression is capable of a negative value, the phase or system is at least *practically* unstable. By this is meant that, although, strictly speaking, an infinitely small disturbance or change may not be sufficient to destroy the equilibrium, yet a very small change in the initial state will be sufficient to do so. The presence of a small portion of matter in a phase for which the above expression has a negative value will in general be sufficient to produce this result. In the case of a system of phases, it is of course supposed that their contiguity is such that the formation of the new phase does not involve any transportation of matter through finite distances.

The preceding criterion affords a convenient point of departure in the discussion of the stability of homogeneous fluids. Of the other forms in which the criterion may be expressed, the following is perhaps the most useful.

If the pressure of a fluid is greater than that of any other phase of its independent variable components which has the same temperature and potentials, the fluid is stable with respect to the formation of any other phase of these components; but if its pressure is not as great as that of some such phase, it will be practically unstable.

Stability of fluids with respect to continuous changes of phase. — In considering the changes which may take place in any mass, we have often to distinguish between infinitesimal changes in existing phases, and the formation of entirely new phases. A phase of a fluid may be stable with respect to the former kind of change, and unstable with respect to the latter. In this case, it may be capable of continued existence in virtne of properties which prevent the commencement of discontinuous changes. But a phase which is unstable with respect to continuous changes is evidently incapable of permanent existence on a large scale except in consequence of passive resistances to change. To obtain the conditions of stability with respect to continuous changes, we have only to limit the application of the variables in (14) to phases adjacent to the given phase. We obtain results of the following nature.

The stability of any phase with respect to continuous changes depends upon the same conditions with respect to the second and higher differential coefficients of the density of energy regarded as a function of the density of entropy and the densities of the several components, which would make the density of energy a minimum, if the necessary conditions with respect to the first differential coefficients were fulfilled.

Again, it is necessary and sufficient for the stability with respect to continuous changes of all the phases within any given limits, that within those limits the same conditions should be fulfilled with respect to the second and higher differential coefficients of the pressure regarded as a function of the temperature and the several potentials, which would make the pressure a minimum, if the necessary conditions with respect to the first differential coefficients were fulfilled.

The equation of the limits of stability with respect to continuous changes may be written

$$(15) \qquad \left(\frac{d\mu_n}{d\gamma_n}\right)_{t,\,\mu_1,\,\ldots\,\mu_{n-1}} = 0, \quad \text{or} \left(\frac{d^2 p}{d\mu_n^2}\right)_{t,\,\mu_1,\,\ldots\,\mu_{n-1}} = \infty,$$

where γ_n denotes the density of the component specified or $m_n \div v$. It is in general immaterial to what component the suffix $_n$ is regarded as relating.

Critical phases. — The variations of two coexistent phases are sometimes limited by the vanishing of the difference between them. Phases at which this occurs are called *critical phases.* A critical phase, like any other, is capable of $n+1$ independent variations, n denoting the number of independently variable components. But when subject to the condition of remaining a critical phase, it is capable of only $n-1$ independent variations. There are therefore two independent equations which characterize critical phases. These may be written

$$(16) \qquad \left(\frac{d\mu_n}{d\gamma_n}\right)_{t,\,\mu_1,\,\ldots\,\mu_{n-1}} = 0, \quad \left(\frac{d^2\mu_n}{d\gamma_n^2}\right)_{t,\,\mu_1,\,\ldots\,\mu_{n-1}} = 0,$$

It will be observed that the first of these equations indent identical with the equation of the limit of stability with respect to continuous changes. In fact, stabile critical phases are situated at that limit. They are also situated at the limit of stability with respect to discontinuous changes. These limits are in general distinct, but touch each other at critical phases.

Geometrical illustrations. — In an earlier paper,*) the author has described a method of representing the thermodynamic properties of substances of invariable composition by means of surfaces. The volume, entropy, and energy of a constant quantity of the substance are represented by rectangular coördinates. This method corresponds to the first kind of fundamental equation described above. Any other kind of fundamental equation for a substance of invariable composition will suggest an analogous geometrical method. In the present paper, the method in which the coördinates represent temperature, pressure, and the potential, is briefly considered. But when the composition of the body in variable, the fundamental equation cannot be completely represented by any surface or finite number of surfaces. In the case of three components, if we regard the temperature and pressure as constant, as well as the total quantity of matter, the relations between ζ, m_1, m_2, m_3 may be represented by a surface in which the distances of a point from the three sides of a triangular prism represent the quantities m_1,

*) Transactions of the Connecticut Academy, vol. ii, part 2.

m_2, m_3, and the distance of the point from the base of the prism represents the quantity ζ. In the case of two components, analogous relations may be represented by a plane curve. Such methods are especially useful for illustrating the combinations and separations of the components, and the changes in states of aggregation, which take place when the substances are exposed in varying proportions to the temperature and pressure considered.

Fundamental equations of ideal gases and gas-mixtures. — From the physical properties which we attribute to ideal gases, it is easy to deduce their fundamental equations. The fundamental equation in ε, η, v, and m for an ideal gas is

$$c \log \frac{\varepsilon - Em}{cm} = \frac{\eta}{m} - H + a \log \frac{m}{v}: \tag{17}$$

that in ψ, t, v, and m is

$$\psi = Em + mt\left(c - H - c \log t + a \log \frac{m}{v}\right): \tag{18}$$

that in p, t, and μ is

$$p = a e^{\frac{H - c - a}{a}} t^{\frac{c + a}{a}} e^{\frac{\mu - E}{at}}, \tag{19}$$

where e denotes the base of the Naperian system of logarithms. As for the other constants, c denotes the specific heat of the gas at constant volume, a denotes the constant value of $pv \div mt$, E and H depend upon the zeros of energy and entropy. The two last equations may be abbreviated by the use of different constants. The properties of fundamental equations mentioned above may easily be verified in each case by differentiation.

The law of Dalton respecting a mixture of different gases affords a point of departure for the discussion of such mixtures and the establishment of their fundamental equations. It is found convenient to give the law the following form:

The pressure in a mixture of different gases is equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its potential.

A mixture of ideal gases which satisfies this law is called an *ideal gas-mixture.* Its fundamental equation in p, t, μ_1, μ_2, etc. is evidently of the form

$$p = \Sigma_1\left(a_1 e^{\frac{H_1 - c_1 - a_1}{a_1}} t^{\frac{c_1 + a_1}{a_1}} e^{\frac{\mu_1 - E_1}{a_1 t}}\right), \tag{20}$$

where Σ_1 denotes summation with respect to the different components of the mixture. From this may be deduced other fundamental equations for ideal gas-mixtures. That in ψ, t, v, m_1, m_2, *etc.* is

(21) $\psi = \Sigma_1\Big(E_1 m_1 + m_1 t\Big(c_1 - H_1 - c_1 \log t + a_1 \log \frac{m_1}{v}\Big)\Big).$

Phases of dissipated energy of ideal gas-mixtures. — When the proximate components of a gas-mixture are so related that some of them can be formed out of others, although not necessarily in the gas-mixture itself at the temperatures considered, there are certain phases of the gas-mixture which deserve especial attention. These are the *phases of dissipated energy*, i. e., those phases in which the energy of the mass has the least value consistent with its entropy and volume. An atmosphere of such a phase could not furnish a source of mechanical power to any machine or chemical engine working within it, as other phases of the same matter might do. Nor can such phases be affected by any catalytic agent. A *perfect catalytic agent* would reduce any other phase of the gas-mixture to a phase of dissipated energy. The condition which will make the energy a minimum is that the potentials for the proximate components shall satisfy an equation similar to that which expresses the relation between the units of weight of these components. For example, if the components were hydrogen, oxygen, and water, since one gram of hydrogen with eight grams of oxygen are chemically equivalent to nine grams of water, the potentials for these substances in a phase of dissipated energy must satisfy the relation

$$\mu_H + 8\mu_O = 9\mu_W.$$

Gas-mixtures with convertible components. — The theory of the phases of dissipated energy of an ideal gas-mixture derives an especial interest from its possible application to the case of those gas-mixtures in which the chemical composition and resolution of the components can take place in the gas-mixture itself, and actually does take place, so that the quantities of the proximate components are entirely determined by the quantities of a smaller number of ultimate components, with the temperature and pressure. These may be called *gas-mixtures with convertible components.* If the general laws of *ideal* gas-mixtures apply in any such case, it may easily be shown that the phases of dissipated energy are the only phases which can exist. We can form a fundamental equation which shall relate solely to these phases. For this end, we first form the equation in p, t, μ_1, μ_2, etc. for the gas-mixture, regarding its proximate components as *not* convertible. This equation will contain a potential for every proximate component of the gas mixture. We then eliminate one (or more) of these potentials by means of the

relations which exist between them in virtue of the convertibility of the components to which they relate, leaving the potentials which relate to those substances which naturally express the ultimate composition of the gas-mixture.

The validity of the results thus obtained depends upon the applicability of the laws of ideal gas-mixtures to cases in which chemical action takes place. Some of these laws are generally regarded as capable of such application, others are not so regarded. But it may be shown that in the very important case in which the components of a gas are convertible at certain temperatures, and not at others, the theory proposed may be established without other assumptions than such as are generally admitted.

It is, however, only by experiments upon gas-mixtures with convertible components, that the validity of any theorie concerning them can be satisfactorily established.

The vapor of the peroxide of nitrogen appears to be a mixture of two different vapors, of one of which the molecular formula is double that of the other. If we suppose that the vapor conforms to the laws of an ideal gas-mixture in a state of dissipated energy, we may obtain an equation between the temperature, pressure, and density of the vapor, which exhibits a somewhat striking agreement with the results of experiment.

Equilibrium of stressed solids. — The second paper commences with a discussion of the conditions of internal and external equilibrium for solids in contact with fluids with regard to all possible states of strain of the solids. These conditions are deduced by analytical processes from the general condition of equilibrium (2). The condition of equilibrium which relates to the dissolving of the solid at a surface where it meets a fluid may be expressed by the equation

$$\mu_1 = \frac{\varepsilon - t\eta + pv}{m}, \tag{22}$$

where ε, η, v, and m_1 denote respectively the energy, entropy, volume, and mass of the solid, if it is homogeneous in nature and state of strain, — otherwise, of any small portion which may be treated as thus homogeneous, — μ_1 the potential in the fluid for the substance of which the solid consists, p the pressure in the fluid and therefore one of the principal pressures in the solid, and t the temperature. It will be observed that when the pressure in the solid is isotropic, the second member of this equation will represent the

potential in the solid for the substance of which it consists [see (9)], and the condition reduces to the equality of the potential in the two masses, just as if it were a case of two fluids. But if the stresses in the solid are not isotropic, the value of the second member of the equation is not entirely determined by the nature and state of the solid, but has in general three different values (for the same salid at the same temperature, and in the same state of strain) corresponding to the three principal pressures in the solid. If a solid in the form of a right parallelopiped is subject to different pressures on its three pairs of opposite sides by fluids in which it is soluble, it is in general necessary for equilibrium that the composition of the fluids shall be different.

The *fundamental equations* which have been described above are limited, in their application to solids, to the case in which the stresses in the solid are isotropic. An example of a more general form of fundamental equation for a solid, is afforded by an epuation between the energy and entropy of a given quantity of the solid, and the quantities which express its state of strain, or by an equation between ψ [see (3)] as determined for a given quantity of the solid, the temperature, and the quantities which expressed the state of strain.

Capillarity. — The solution of the problems which precede may be regarded as a first approximation, in which the peculiar state of thermodynamic equilibrium about the surfaces of discontinuity is neglected. To take account of the condition of things at these surfaces, the following method is used. Let us suppose that two homogeneous fluid masses are separated by a surface of discontinuity, i. e., by a very thin non-homogeneous film. Now me may imagine a state of things in which each of the homogeneous masses extends without variation of the densities of its several components, or of the densities of energy and entropy, quite up to a geometrical surface (to be called the dividing surface) at which the masses meet. We may suppose this surface to be sensibly coincident with the physical surface of discontinuity. Now if we compare the actual state of things with the supposed state, there will be in the former in the vicinity of the surface a certain (positive or negative) excess of energy, of entropy, and of each of the component substances. These quantities are denoted by ε^S, η^S, m_1^S, m_2^S, etc. and are treated as belonging to the surface. The ^{S} is used simply as a distinguishing mark, and must not be taken for an algebraic exponent.

It is shown that the conditions of equilibrium already obtained relating to the temperature and the potentials of the homogeneous masses, are not affected by the surfaces of discontinuity, and that the complete value of $d\varepsilon^S$ is given by the equation

$$(23) \qquad \delta\varepsilon^S = t\delta\eta^S + \sigma\delta s + \mu_1\delta m_1^S + \mu_2\delta m_2^S + \text{etc.}$$

in which s denotes the area of the surface considered, t the temperature, μ_1, μ_2, etc. the potentials for the various components in the adjacent masses. It may be, however, that some of the components are found only at the surface of discontinuity, in which case the letter μ with the suffix relating to such a substance denotes, as the equation shows, the rate of increase of energy at the surface per unit of the substance added, when the entropy, the area of the surface, and the quantities of the other components are unchanged. The quantity σ we may regard as defined by the equation itself, or by the following, which is obtained by integration:

$$(24) \qquad \varepsilon^S = t\eta^S + \sigma s + \mu_1 m_1^S + \mu_2 m_2^S + \text{etc.}$$

There are terms relating to variations of the curvatures of the surface which might be added, but it is shown that we can give the dividing surface such a position as to make these terms vanish, and it is found convenient to regard its position as thus determined. It is always sensibly coincident with the physical surface of discontinuity. (Yet in treating of plane surfaces, this supposition in regard to the position of the dividing surface is unnecessary, and it is sometimes convenient to suppose that its position is determined by other considerations.)

With the aid of (23), the remaining condition of equilibrium for contiguous homogeneous masses is found, viz:

$$(25) \qquad \sigma(c_1 + c_2) = p' - p'',$$

where p', p'' denote the pressures in the two masses, and c_1, c_2 the principal curvatures of the surface. Since this equation has the same form as if a tension equal to σ resided at the surface, the quantity σ is called (as is usual) the *superficial tension*, and the dividing surface in the particular position above mentioned is called the *surface of tension.*

By differentiation of (24) and comparison with (23), we obtain

$$(26) \qquad d\sigma = -\eta_S\, dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \text{etc.},$$

where η_S, Γ_1, Γ_2, etc., are written for $\frac{\eta^S}{s}$, $\frac{m_1^S}{s}$, $\frac{m_1^S}{s}$, etc., and de-

note the superficial densities of entropy and of the various substances. We may regard σ as a function of t, μ_1, μ_2, etc., from which if known η_S, Γ_1, Γ_2, etc. may be determined in terms of the same variables. An equation between σ, t, μ_1, μ_2, etc. may therefore be called a *fundamental equation for the surface of discontinuity*. The same may be said of an equation between ε_S, η_S, s, m_1^S, m_2^S, etc.

It is necessary for the stability of a surface of discontinuity that its tension shall be as small as that of any other surface which can exist between the same homogeneous masses with the same temperature and potentials. Beside this condition, which relates to the nature of the surface of discontinuity, there are other conditions of stability, which relate to the possible motion of such surfaces. One of these is that the tension shall be positive. The others are of a less simple nature, depending upon the extent and form of the surface of discontinuity, and in general upon the whole system of which it is a part. The most simple case of a system with a surface of discontinuity is that of two coëxistent phases separated by a spherical surface, the outer mass being of indefinite extent. When the interior mass and the surface of discontinuity are formed entirely of substances which are components of the surrounding mass, the equilibrium is always unstable; in other cases, the equilibrium may be stable. Thus, the equilibrium of a drop of water in an atmosphere of vapor is unstable, but may be made stable by the addition of a little salt. The analytical conditions which determine the stability or instability of the system are easily found, when the temperature and potentials of the system are regarded as known, as well as the fundamental equations for the interior mass and the surface of discontinuity.

The study of surfaces of discontinuity throws considerable light upon the subject of the stability of such phases of fluids as have a less pressure than other phases of the same components with the same temperature and potentials. Let the pressure of the phase of which the stability is in question be denoted by p', and that of the other phase of the same temperature and potentials by p''. A spherical mass of the second phase and of a radius determined by the equation

$$2\sigma = (p'' - p')r, \tag{27}$$

would be in equilibrium with a surrounding mass of the first phase.

This equilibrium, as we have just seen, is instable, when the surrounding mass is indefinitely extended. A spherical mass a little larger would tend to increase indefinitely. The work required to form such a spherical mass, by a reversible process, in the interior of an infinite mass of the other phase, is given by the equation

$$W = \sigma s - (p'' - p')v''. \tag{28}$$

The term σs represents the work spent in forming the surface, and the term $(p'' - p')v''$ the work gained in forming the interior mass. The second of these quantities is always equal to two-thirds of the first. The value of W is therefore positive, and the phase is in strictness stable, the quantity W affording a kind of measure of its stability. We may easily express the value of W in a form which does not involve any geometrical magnitudes, viz:

$$W = \frac{16\pi\sigma^3}{3(p'' - p')^2}, \tag{29}$$

where p'', p' and σ may be regarded as functions of the temperature and potentials. It will be seen that the stability, thus measured, is infinite for an infinitesimal difference of pressures, but decreases very rapidly as the difference of pressures increases. These conclusions are all, however, practically limited to the case in which the value of r, as determined by equation (27) is of sensible magnitude.

With respect to the somewhat similar problem of the stability of the surface of contact of two phases with respect to the formation of a new phase, the following results are obtained. Let the phases (supposed to have the same temperature and potentials) be denoted by A, B and C; their pressures by p_A, p_B and p_C; and the tensions of the three possible surfaces σ_{AB}, σ_{BC}, σ_{AC}. If p_C is less than

$$\frac{\sigma_{BC} p_A + \sigma_{AC} p_B}{\sigma_{BC} + \sigma_{AC}},$$

there will be no tendency toward the formation of the new phase at the surface between A and B. If the temperature or potentials are now varied until p_C is equal to the above expression, there are two cases to be distinguished. The tension σ_{AB} will be either equal to $\sigma_{AB} + \sigma_{BC}$ or less. (A greater value could only relate to an unstable and therefore unusual surface.) If $\sigma_{AB} = \sigma_{AC} + \sigma_{BC}$, a farther variation of the temperature or potentials, making p_C greater than the above expression, would cause the phase C to be formed at

the surface between A and B. But if $\sigma_{AB} < \sigma_{AC} + \sigma_{BC}$, the surface between A and B would remain stable, but with rapidly diminishing stability, after p_C has passed the limit mentioned.

The conditions of stability for a line where several surfaces of discontinuity meet, with respect to the possible formation of a new surface, are capable of a very simple expression. If the surfaces A-B, B-C, C-D D-A, separating the masses A, B, C, D, meet along a line, it is necessary for equilibrium that their tensions and directions at any point of the line should be such that a quadrilateral α, β, γ, δ may be formed with sides representing in direction and length the normals and tensions of the successive surfaces. For the stability of the system with reference to the possible formation of surfaces between A and C, or between B and D, it is farther necessary that the tensions σ_{AC} and σ_{BD} should be greater than the diagonals $\alpha\gamma$ and $\beta\delta$ respectively. The conditions of stability are entirely analogous in the case of a greater number of surfaces. For the conditions of stability relating to the formation of a new phase at a line in which three surfaces of discontinuity meet, or at a point where four different phases meet, the reader is referred to the original paper.

Liquid films. — When a fluid exists in the form of a very thin film between other fluids, the great inequality of is extension in different directions will give rise to certain peculiar properties, even when its thickness is sufficient for its interior to have the properties of matter in mass. The most important case is where the film is liquid and the contiguous fluids are gaseous. If we imagine the film to be divided into elements of the same order of magnitude as its thickness, each element extending through the film from side to side, it is evident that far less time will in general be required for the attainment of approximate equilibrium between the different parts of any such element and the contiguous gases than for the attainment of equilibrium between all the different elements of the film.

There will accordingly be a time, commencing shortly after the formation of the film, in which its separate elements may be regarded as satisfying the conditions of internal equilibrium, and of equilibrium with the contiguous gases, while they may not satisfy all the conditions of equilibrium with each other. It is when the changes due to this want of complete equilibrium take place so slowly that the film appears to be at rest, except so far as it

accommodates itself to any change in the external conditions to which it is subjected, that the characteristic properties of the film are most striking and most sharply defined. It is from this point of view that these bodies are discussed. They are regarded as satisfying a certain welldefined class of conditions of equilibrium, but as not satisfying at all certain other conditions which would be necessary for complete equilibrium, in consequence of which they are subject to gradual changes, which ultimately determine their rupture.

The elasticity of a film (i. e., the increase of its tension when extended), is easily accounted for. It follows from the general relations given above that, when a film has more than one component, those components which diminish the tension will be found in greater proportion on the surfaces. When the film is extended, there will not be enough of these substances to keep up the same volume- and surface-densities as before, and the deficiency will cause a certain increase of tension. It does not follow that a thinner film has always a greater tension than a thicker formed of the same liquid. When the phases within the films as well as without are the same, and the surfaces of the films are also the same, there will be no difference of tension. Nor will the tension of the same film be altered, if a part of the interior drains away in the course of time, without affecting the surfaces. If the thickness of the film is reduced by evaporation, its tension may be either increased or diminished, according to the relative volatility of its different components.

Let us now suppose that the thickness of the film is reduced until the limit is reached at which the interior ceases to have the properties of matter in mass. The elasticity of the film, which determines its stability with respect to extension and contraction, does not vanish at this limit. But a certain kind of instability will generally arise, in virtue of which inequalities in the thickness of the film will tend to increase through currents in the interior of the film. This probably leads to the destruction of the film, in the case of most liquids. In a film of soap-water, the kind of instability described seems to be manifested in the breaking out of the black spots. But the sudden diminution in thickness which takes place in parts of the film is arrested by some unknown cause, possibly by viscous or gelatinous properties, so that the rupture of the film does not necessarily follow.

Electromotive force. — The conditions of equilibrium may be modified by electromotive force. Of such cases a galvanic or electrolytic cell may be regarded as the type. With respect to the potentials for the ions and the electrical potential the following relation may be noticed:

When all the conditions of equilibrium are fulfilled in a galvanic or electrolytic cell, the electromotive force is equal to the difference in the values of the potential for any ion at the surfaces of the electrodes multiplied by the electro-chemical equivalent of that ion, the greater potential of an anion being at the same electrode as the greater electrical potential, and the reverse being true of a cation.

The relation which exists between the electromotive force of a *perfect electro-chemical apparatus* (i. e., a galvanic or electrolytic cell which satisfies the condition of reversibility), and the changes in the cell which accompany the passage of electricity, may be expressed by the equation

$$(30) \qquad d\varepsilon = (V' - V'')\,de + t\,d\eta + d\,W_G + d\,W_P,$$

in which $d\varepsilon$ denotes the increment of the intrinsic energy in the apparatus, $d\eta$ the increment of entropy, de the quantity of electricity which passes trough it, V' and V'' the electrical potentials in pieces of the same kind of metal connected with the anode and cathode respectively, $d\,W_G$ the work done by gravity, and $d\,W_P$ the work done by the pressures which act on the external surface of the apparatus. The term $d\,W_G$ may generally be neglected. The same is true of $d\,W_P$, when gases are not concerned. If no heat is supplied or withdrawn the term $t\,d\eta$ will vanish. But in the calculation of electromotive forces, which is the most important application of the equation, it is convenient and customary to suppose that the temperature is maintained constant. Now this term $t\,d\eta$, which represents the heat absorbed by the cell, is frequently neglected in the consideration of cells of which the temperature is supposed to remain constant. In other words, it is frequently assumed that neither heat or cold is produced by the passage of an electrical current through a perfect electro-chemical apparatus (except that heat which may be indefinitely diminished by increasing the time in which a given quantity of electricity passes), unless it be by processes of a secondary nature, which are not immediately or necessarily connected with the process of electrolysis.

That this assumption is incorrect is shown by the electromotive force of a gas battery charged with hydrogen and nitrogen,

by the currents caused by differences in the concentration of the electrolyte, by electrodes of zinc and mercury in a solution of sulphate of zinc, by *a priori* considerations based on the phenomena exhibited in the direct combination of the elements of water or of hydrochloric acid, by the absorption of heat which M. Favre has in many cases observed in a galvanic or electrolytic cell, and by the fact that the solid or liquid state of an electrode (at its temperature of fusion) does not affect the electromotive force.

J. W. Gibbs.

Pappi Alexandrini collectionis quae supersunt e libris manu scriptis edidit, Latina interpretatione et commentariis instruxit Fridericus Hultsch. (Volumen I, enthaltend die Ueberreste von Buch 2—5, Berlin, Weidmannsche Buchhandlung 1876; Volumen II, enthaltend Buch 6 und 7, 1877; Voluminis III tomus I, enthaltend die Ueberreste des 8. Buches und verschiedene Supplemente, tomus II, enthaltend die Indices, 1878.

Die hohe Bedeutung, welche die mathematische Sammlung des Pappus von Alexandria als Quellenwerk auch für die neuere mathematische Forschung hat, ist zu keiner Zeit seit dem Wiedererwachen der Wissenschaften verkannt worden. Nachdem Commandini im J. 1588[1]) seine lateinische Uebersetzung nebst ausführlichen Commentaren veröffentlicht hatte, verbreitete sich eine gewisse, freilich nur lückenhafte Kenntniss von dem Inhalte des Werkes bei den Forschern auf historisch-mathematischem Gebiete. Mehr als hundert Jahre waren seit dem Erscheinen der Commandinischen Bearbeitung vergangen, als die Erinnerung an Pappus von neuem wachgerufen und das Studium des Originaltextes zum erstenmale versucht wurde von Wallis und Halley.[2]) Insbesondere zeigte der letztere in seiner Ausgabe der Sectio rationis (*λόγου ἀποτομή*) und der Conica des Apollonius allenthalben, welche Wichtigkeit die Lemmen des Pappus für das Verständniss des Apollonius haben. Hierauf folgte die Re-

1) Das Jahr 1588 ist angegeben auf der Vorderseite des letzten Blattes. Der Titel trägt die Jahreszahl 1589. Bald darauf ist genau dieselbe Ausgabe unter anderem Titelblatt und mit der Jahreszahl 1602 zum Verkauf gestellt worden. Vergl. vol. I des hier besprochenen Werkes, Praefatio p. XVII.

2) Vergl. vol. I praef. p. XIX. XXI f.